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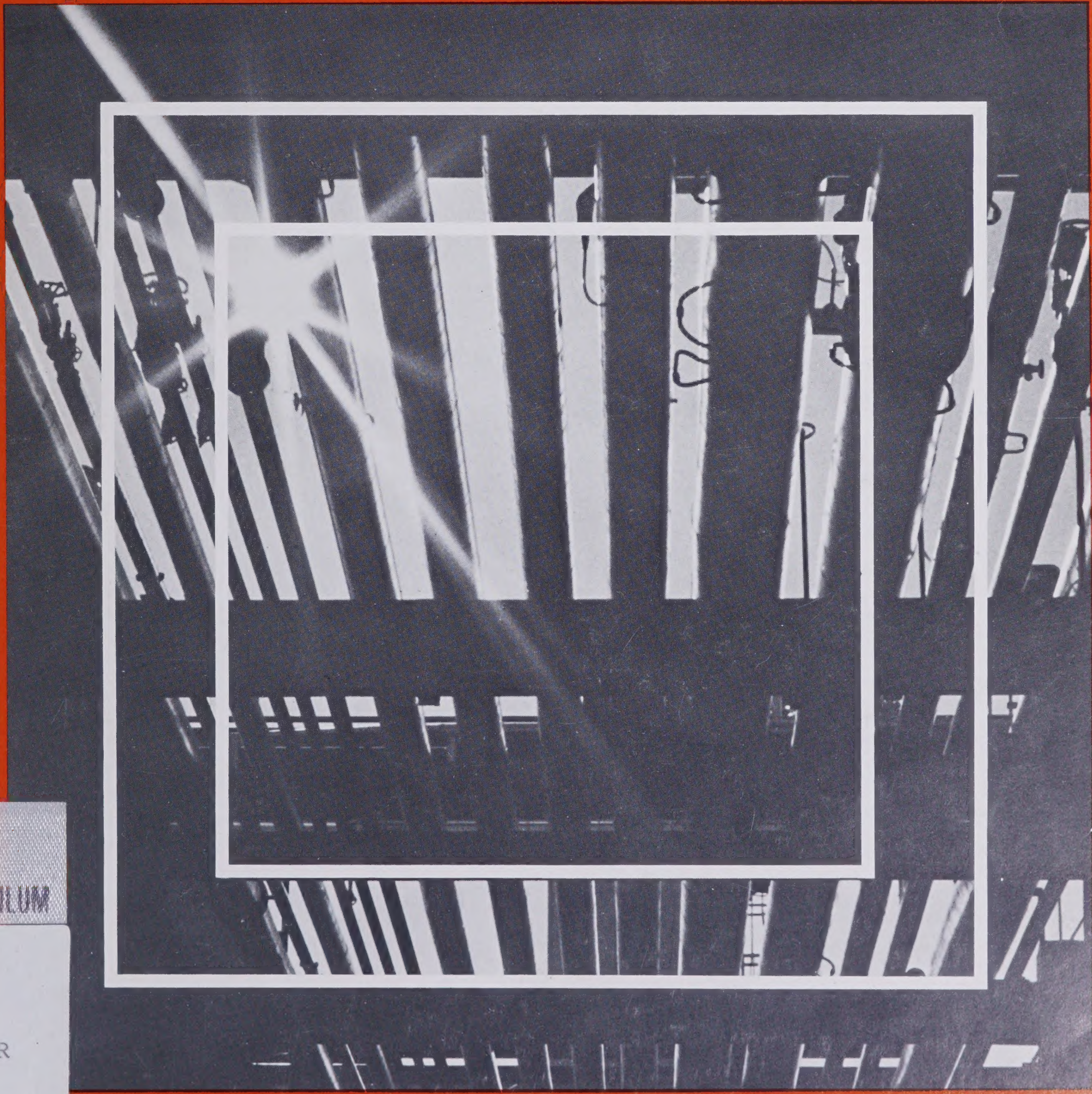
# The Athabasca Tar Sands

an *ALCHEM* elective unit



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Syncrude Educational Services Division provides students and teachers with factual information of an educational nature on the development of the Athabasca Oil Sands.

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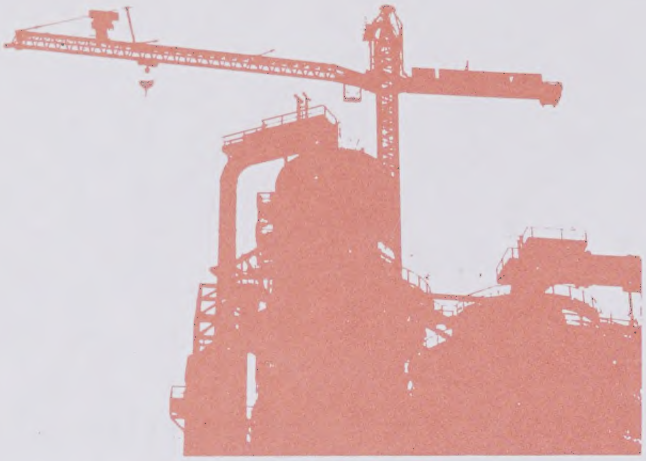

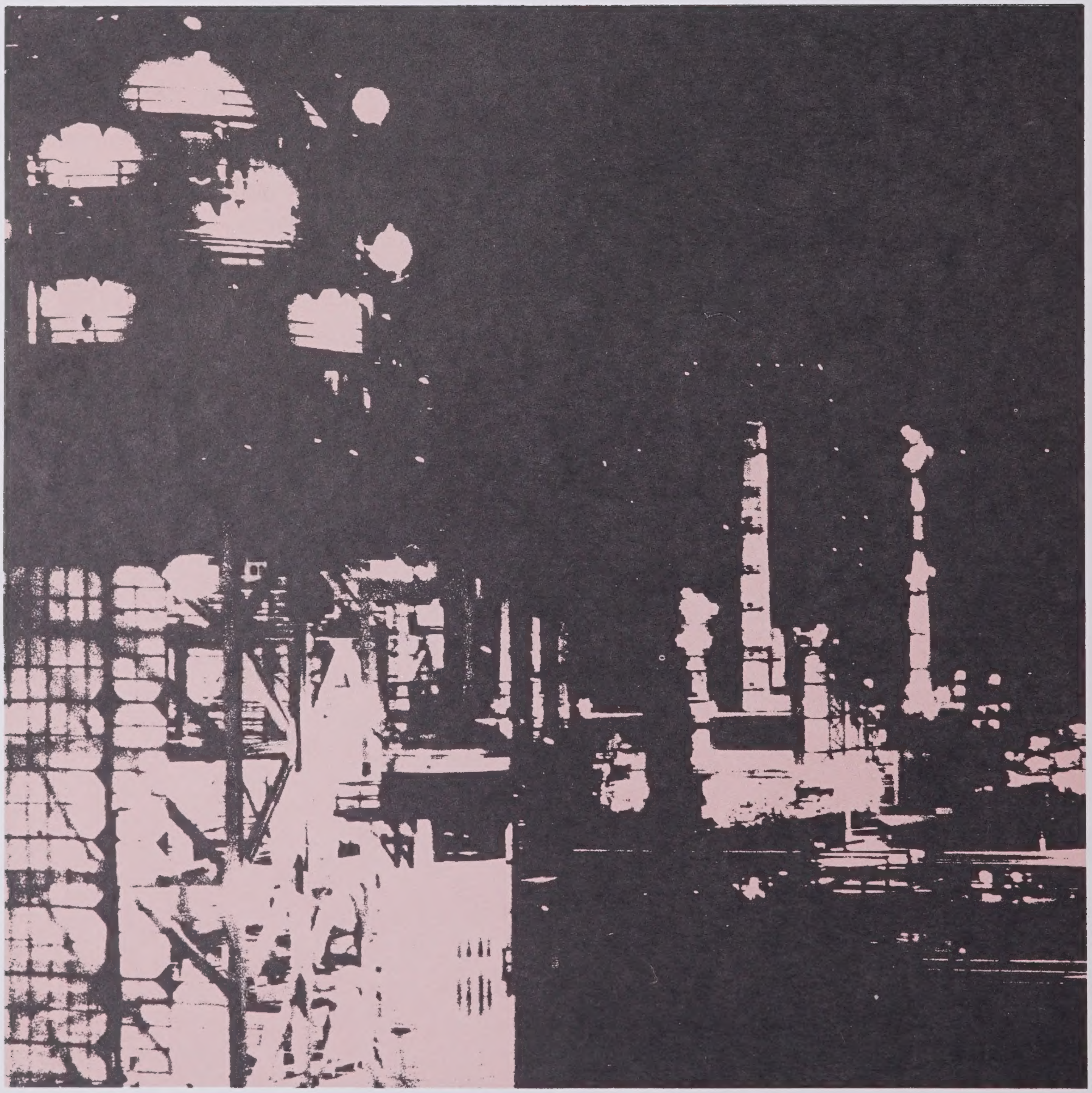

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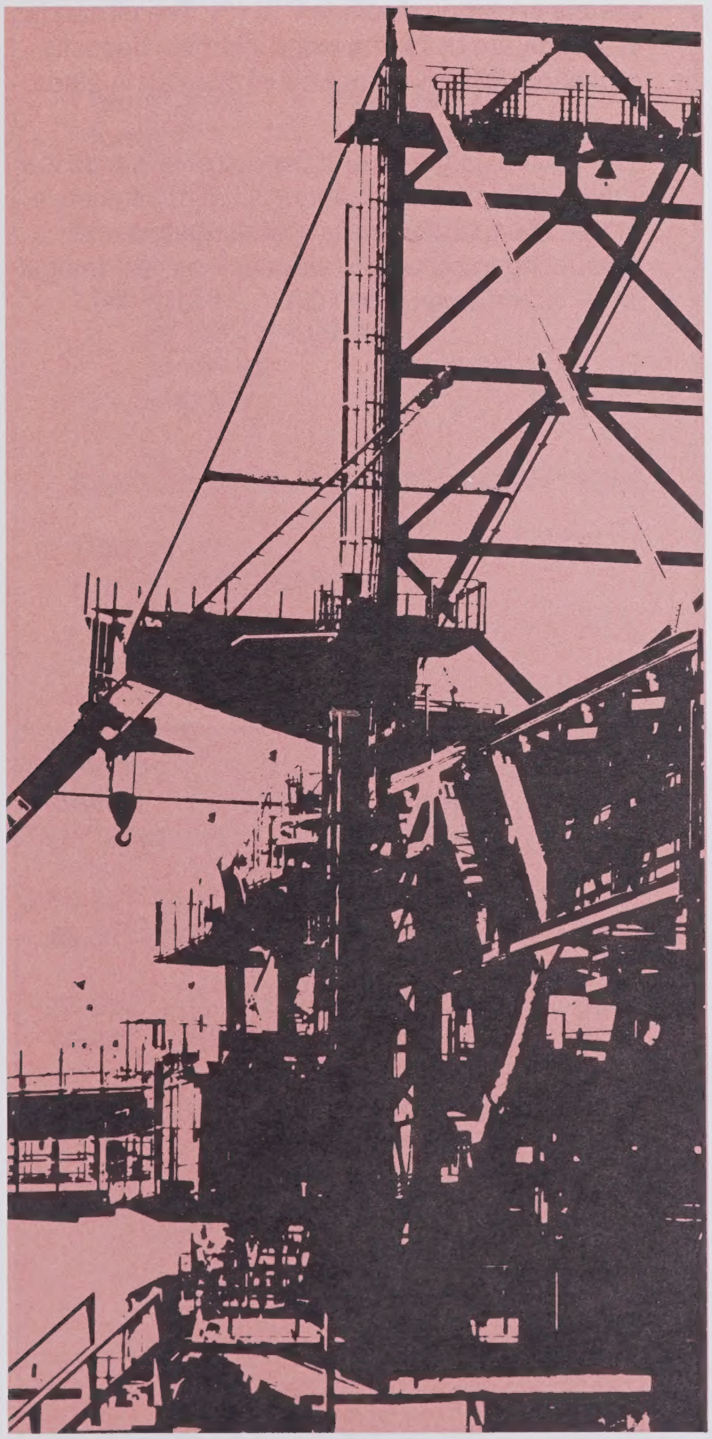
The Athabasca Tar Sands

# Relative Importance and Extent of Energy Resources



## Importance of Energy Resources

In Canada, as in the rest of the world, public awareness of the importance of fossil fuels has increased greatly in the past few years. The rapid increase in the price of crude petroleum has emphasized some points about energy sources in general.

1. A technological society is predicated upon a constantly increasing supply of energy.
2. By far the largest energy source for industrial nations is fossil fuel, particularly petroleum.
3. Cheap fossil fuel, again particularly petroleum, is in limited supply. Alternative energy sources must be developed now.

Canada has the potential to be self-sufficient in petroleum, and is consequently in a very enviable economic position. To attain self-sufficiency with our energy requirements increasing and our conventional petroleum reserves decreasing annually, development of energy sources such as the oil sands becomes essential.

Present energy use in Canada is about 46% petroleum, 26% hydroelectric, 19% natural gas, 7.5% coal and 1.5% nuclear. Canada's total energy use in 1975 was 8.29 exajoules (EJ) (exa(E) = $10^{18}$).

## Nuclear and Hydroelectric Energy

According to current estimates, Canada's total energy demand will more than double by the year 2000. Although nuclear technology is well developed in Canada, and will account for a greater percentage of our energy supply in future, fossil fuels will continue to be the major energy source.

Hydroelectric energy supply is limited by the number of locations where a river can be dammed. Another limiting factor is that electricity cannot be transported over long distances efficiently.

## Fossil Fuels

Fossil fuels include natural gas, crude oil, coal, oil shales and oil sands. Natural gas and crude oil are extensively developed now. Only a small fraction of Alberta's immense coal reserves are currently being used.

### Oil Shale

Oil shale deposits are solid sedimentary layers containing an insoluble form of solid organic materials called *kerogens*. Kerogens decompose into liquid hydrocarbons on heating. The major oil shale deposits exist in the Colorado area of the United States (about 2 trillion barrels) and Brazil (about 800 billion barrels). These figures refer to organic material in place in the ground, and may be very different from recoverable amounts.

Extracting oil from shales is costly and difficult, and no large commercial processes were in operation as of 1978. In the United States, however, several companies are committed to commercial development of oil shale. With current sources, the United States faces a shortfall of energy supply of nearly one-third by the year 2000, which makes development of oil shales economically inevitable.

### Oil Sands

Oil sands are sedimentary layers of loose particles impregnated with bitumen. Bitumen is a very viscous hydrocarbon mixture which is totally soluble in carbon disulfide $CS_2$ ($\ell$). The oil sands in Alberta are by far the world's largest deposits with about 900 billion barrels of bitumen in place.

The second largest world deposit of oil sands is in Venezuela, containing about 30 Gt of bitumen in place. The third largest is in Madagascar, amounting to about 300 megatonnes (Mt) (mega (M) = $10^6$ or about 0.300 Gt).

| Geographic Area | Year | Coal | Oil | Natural Gas | Hydro-electric | Nuclear | Energy Used (x $10^{18}$ J) |
|---|---|---|---|---|---|---|---|
| Canada | 1960 | 15.0 | 49 | 9 | 28.0 | | 3.89 |
| | 1975 | 7.5 | 46 | 19 | 26.0 | 1.5 | 8.29 |
| North America | 1950 | 5.1 | 60 | 28 | 7.5 | | 22.70 |
| | 1975 | 2.1 | 46 | 39 | 9.3 | 3.2 | 59.00 |
| World | 1950 | 7.5 | 64 | 18 | 10.0 | | 34.70 |
| | 1975 | 1.7 | 65 | 22 | 8.7 | 2.2 | 146.00 |

**World excludes U.S.S.R. block and China**

*Table 1: Percentage Distribution of Energy Resources*

**Note:**

Conversion to SI measurement will change the standard liquid petrochemical measure from barrels to tonnes.

**1 barrel (bbl)** = **159 litres ($\ell$)**
**1 tonne (t)** = **1000 kilograms (kg)**

**Bitumen (Density = 1.00 kg/$\ell$)**

$$\begin{aligned} 1\ \text{bbl} &= 159\ \ell \\ &= 159\ \ell \times 1.00\ \text{kg}/\ell \\ &= 159\ \text{kg} \\ &= 0.159\ \text{t} \end{aligned}$$

**Synthetic Crude Oil (Density = 0.875 kg/$\ell$)**

$$\begin{aligned} 1\ \text{bbl} &= 159\ \ell \\ &= 159\ \ell \times 0.875\ \text{kg}/\ell \\ &= 139\ \text{kg} \\ &= 0.139\ \text{t} \end{aligned}$$

**Example:**

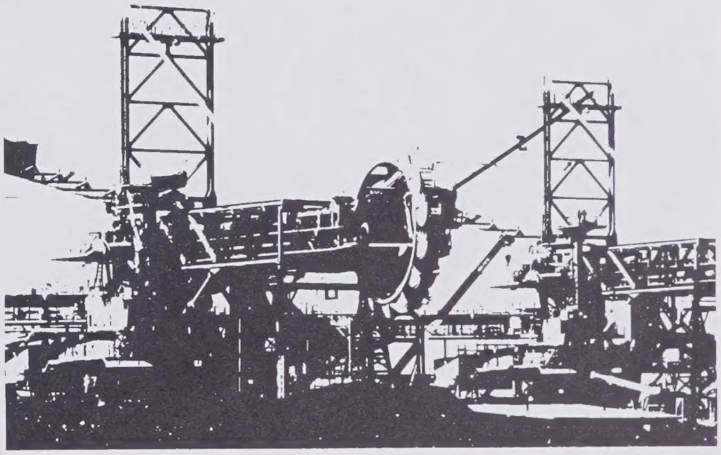
Alberta reserves of bitumen in place.

$$\begin{aligned} &900 \times 10^9\ \text{bbl} \times 159\ \ell/\text{bbl} \times 1.00\ \text{kg}/\ell \\ &\quad = 143\,000 \times 10^9\ \text{kg} \\ &\quad = 143 \times 10^{12}\ \text{kg} \times 1\ \text{t}/10^3\ \text{kg} \\ &\quad = 143 \times 10^9\ \text{t} \\ &\quad = 143\ \text{Gt} \end{aligned}$$

Alberta oil sands contain about 143 gigatonnes (Gt) of bitumen (giga (G) = $10^9$).

**Synthetic Crude Oil**

Synthetic crude is a product extracted from bitumen comparable in composition, viscosity and energy content to conventional crude oil. Of the 143 Gt of bitumen in place in Alberta (equal to about 106 Gt of synthetic crude), it is expected that 35 Gt of synthetic crude oil will ultimately be recovered from Alberta's oil sands. According to the Alberta Energy Resources Conservation Board (ERCB) estimate, the economically surface-mineable deposits in the Athabasca sands alone total 3.7 Gt of recoverable synthetic crude. This compares to Canada's total estimated recoverable reserves of conventional crude of about 1.2 Gt. Put another way, 3.7 Gt of synthetic crude would equal 50 times Canada's current annual petroleum consumption. Allowing a 5 per cent per year increase in energy consumption, this amount could supply Canada's petroleum needs for 25 years.



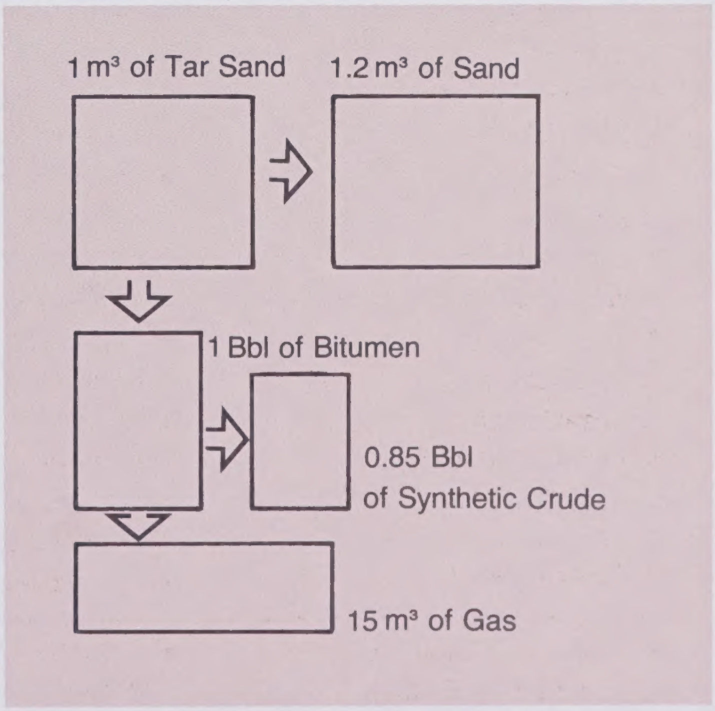
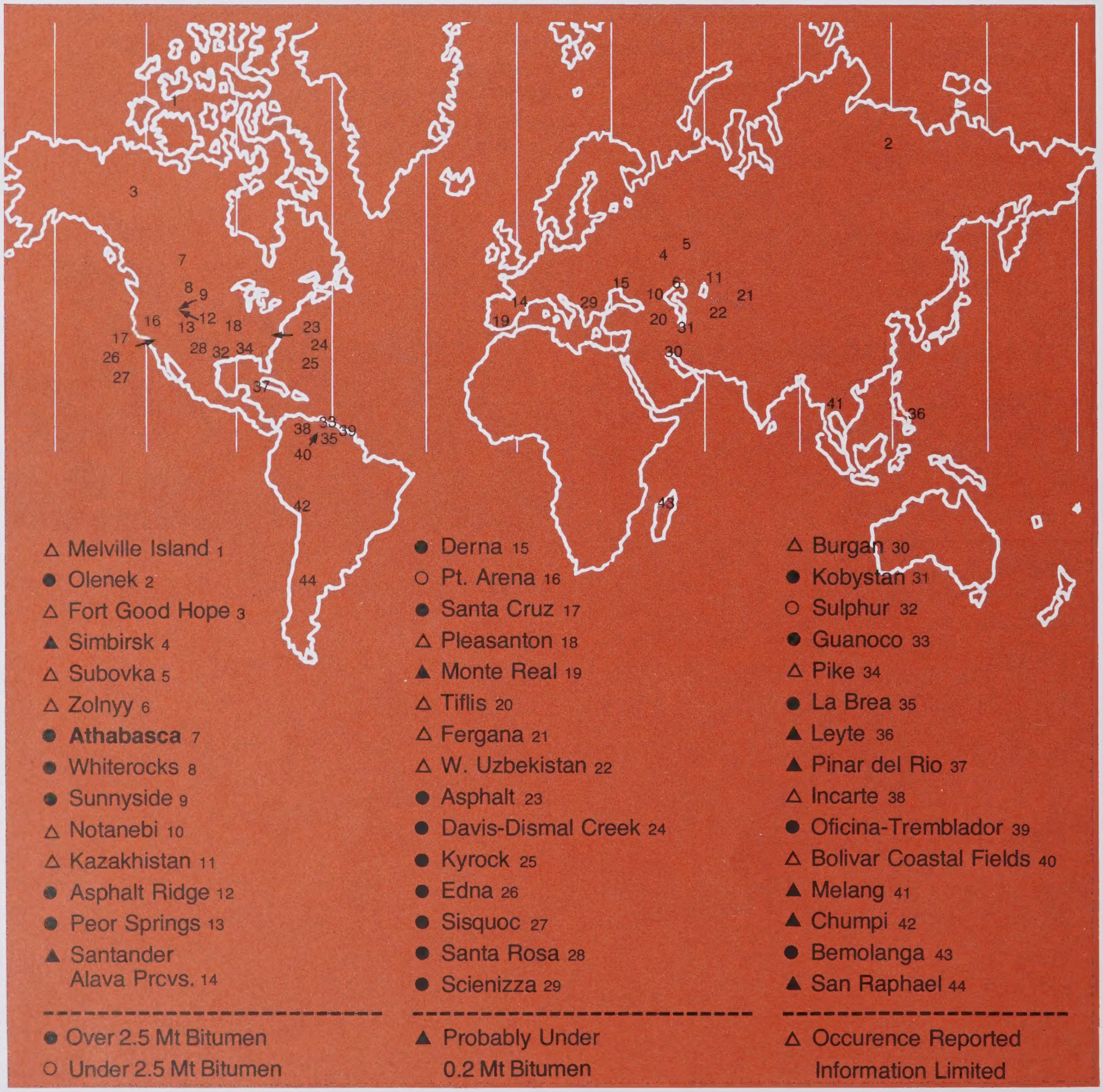


*Figure 1*



△ Melville Island 1
● Olenek 2
△ Fort Good Hope 3
▲ Simbirsk 4
△ Subovka 5
△ Zolnyy 6
● **Athabasca** 7
● Whiterocks 8
● Sunnyside 9
△ Notanebi 10
△ Kazakhistan 11
● Asphalt Ridge 12
● Peor Springs 13
▲ Santander
Alava Prcvs. 14

● Derna 15
○ Pt. Arena 16
● Santa Cruz 17
△ Pleasanton 18
▲ Monte Real 19
△ Tiflis 20
△ Fergana 21
△ W. Uzbekistan 22
● Asphalt 23
● Davis-Dismal Creek 24
● Kyrock 25
● Edna 26
● Sisquoc 27
● Santa Rosa 28
● Scienizza 29

△ Burgan 30
● Kobystan 31
○ Sulphur 32
● Guanoco 33
△ Pike 34
● La Brea 35
▲ Leyte 36
▲ Pinar del Rio 37
△ Incarte 38
● Oficina-Tremblador 39
△ Bolivar Coastal Fields 40
▲ Melang 41
▲ Chumpi 42
● Bemolanga 43
▲ San Raphael 44

● Over 2.5 Mt Bitumen
○ Under 2.5 Mt Bitumen

▲ Probably Under
0.2 Mt Bitumen

△ Occurence Reported
Information Limited

***Figure 2: Location & Extent of Tar and Oil Sands Deposits in the World***

# Geography and Geology

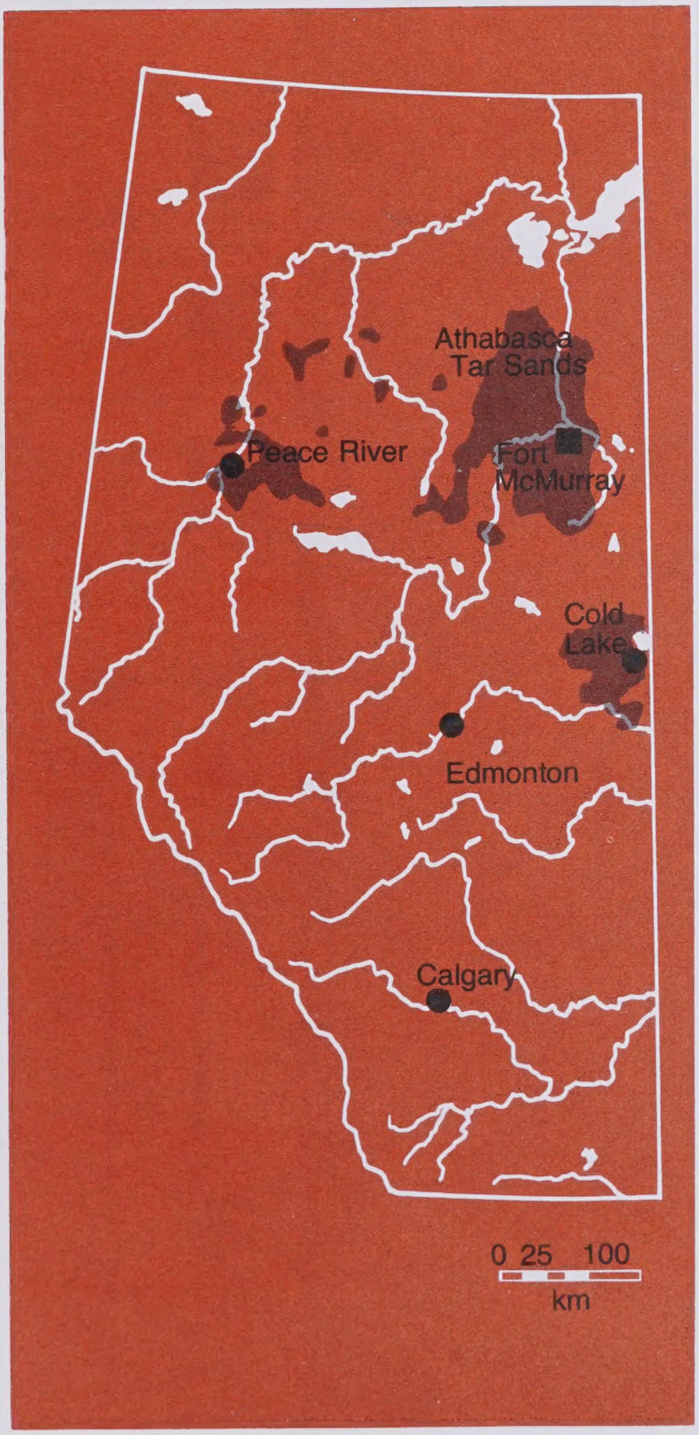


*Figure 3: Location of Tar and Oil Sand Deposits in Alberta*

### Geography

Although Canada can lay claim to the world's largest single oil sands deposit, major deposits also occur in South America, Africa, U.S.A., Europe and U.S.S.R. as shown in Figure 2.

The oil sands in Alberta underlie an area of some 50 000 km² primarily in four major deposits as shown in Figure 3.

The largest and best-known is the Athabasca deposit, extending over some 30 000 km². About 10% of the oil sands in this deposit lie under less than 50 m of soil and rock cover (overburden). This 10% is economically surface-mineable by conventional methods. (The term tar sand refers specifically to the Athabasca deposit. Oil sand is a more general term referring to any deposit of very heavy crude petroleum or bitumen.)

## Geography of Athabasca Deposit

The bitumen-saturated layer of the Athabasca deposit (see Figure 4) averages 30 m thick (ranging from 6 - 90 m) and has an average of 12% (ranging from 1 - 18%) bitumen, by mass. This layer is covered by 0 to 750 m of overburden, depending on which deposit and which location is examined. The Athabasca deposit includes about 2 x $10^5$ hectares (ha) with less than 50 m and about 2 x $10^6$ ha with from 50 - 600 m of overburden. (1 hectare is an area about one football field square, or 100 m x 100 m, or $10^4$ $m^2$.)

## Geology

The geological formations (strata) containing bitumen date from lower Cretaceous period, and rest on an eroded limestone layer dating from the upper Devonian period. The Devonian layer beneath the oil sand formations is about 300 million years old. The Cretaceous layers containing bitumen cannot be dated accurately, but they are between 100 and 200 million years old.

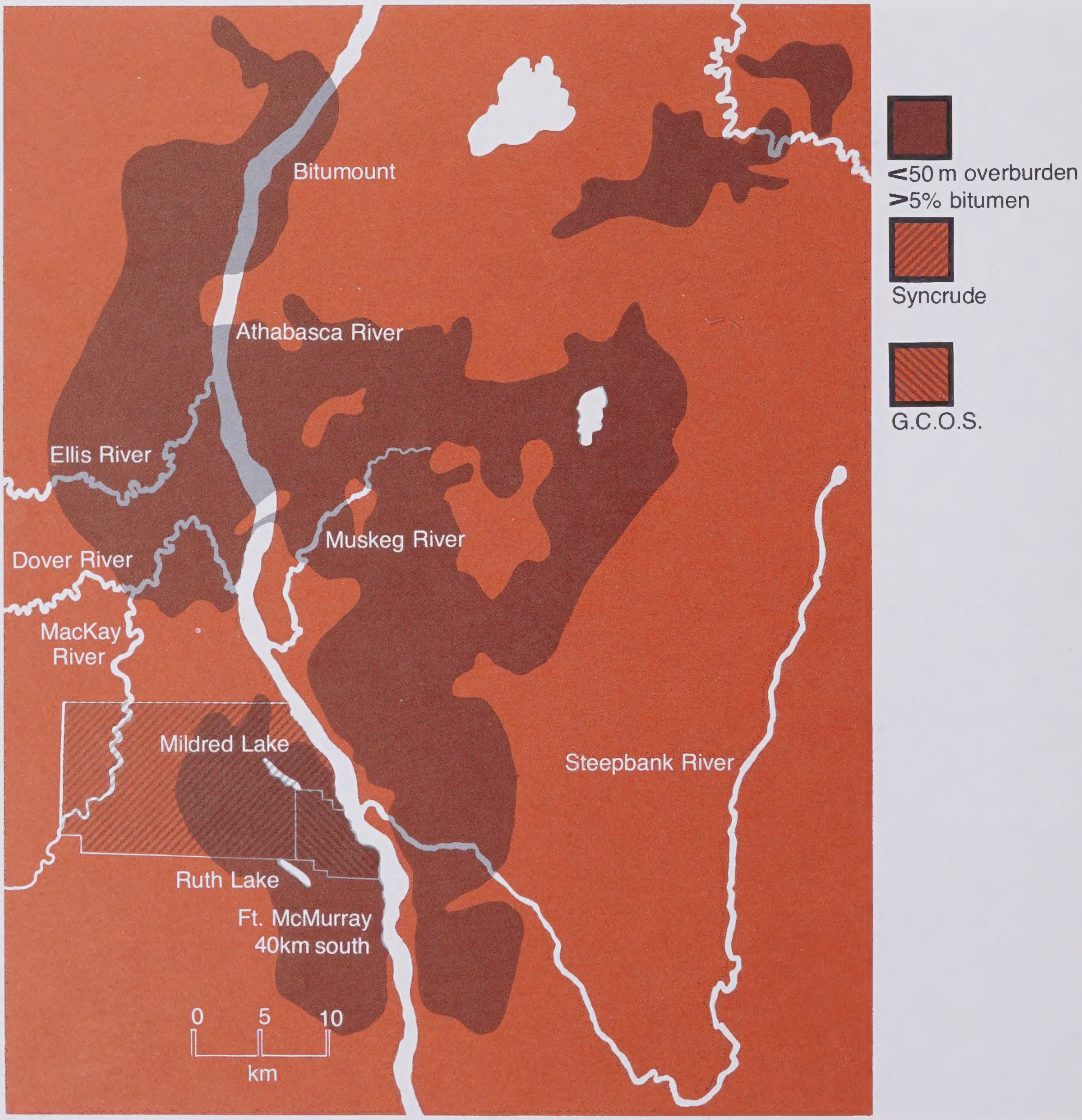


*Figure 4: Athabasca Deposit — Economically Surface Mineable Area*

The date of formation of the bitumen itself is not well established. It is considered a young crude oil in the sense that hydrocarbon deposits become more fluid with time.

Geochemical theories about oil sands are still open to question, however. One theory holds that bitumen was formed at the same time as the strata it occupies. Another holds that it formed elsewhere and migrated into these layers, losing its volatile (easily vaporized) component as it did so. The former theory or *autochthonous* theory is currently more popular, but no good hard evidence exists either way. In fact, such evidence as does exist only complicates matters. Whereas crude oil deposits are accepted as marine in origin, the oil sands may be a fresh water organism formation. While the amount of bitumen and the type of sediment it occupies vary greatly throughout the deposits, the chemical composition of the bitumen is remarkably uniform.

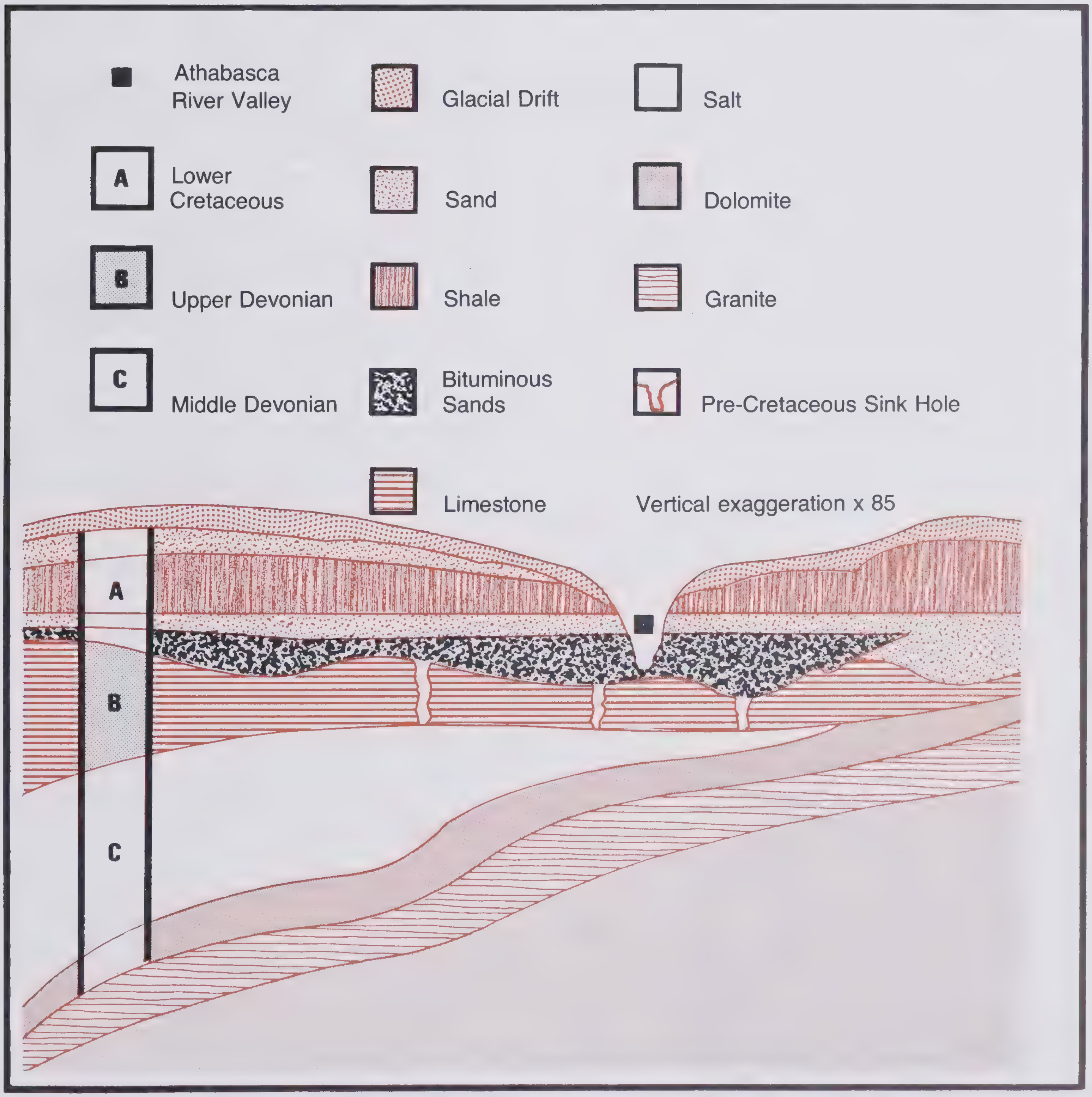


*Figure 5: Geological Stratification of the Athabasca Deposit*

# Composition of Athabasca Deposit

### Physical Composition

The Athabasca sand layer is essentially composed of quartz ($SiO_2$) sand grains of which 99.9% are less than 1 mm in size. Each grain is surrounded by a film of water, which in turn is surrounded by a film of bitumen. Void spaces between grains are mostly water filled. The water contains traces of very fine mineral particles. These are extremely small particles of a wide variety of rock-forming materials and compounds.

The average composition of oil sand is about 84% sand, 12% bitumen and 4% water, by mass. These values all vary over wide ranges.

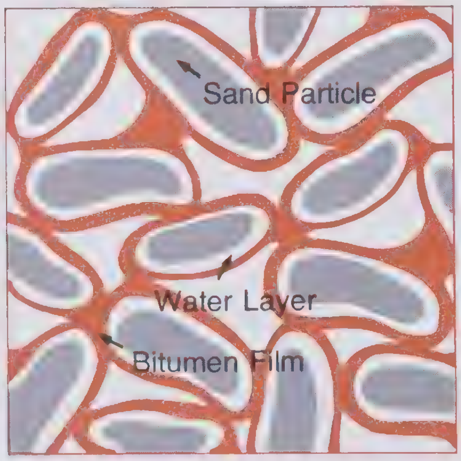


*Figure 6: Physical Composition of Oil Sand*

### Chemical Composition of Bitumen

The bitumen composition is shown below in an example of a typical analysis. Unlike the physical composition these values are remarkably similar throughout the oil sands.

About 50% of a bitumen sample will distill at standard pressure (101 kPa) without cracking (without large molecules decomposing into smaller ones). About three-fifths of this distilled fraction is light aromatic compounds and two-fifths is an alkane mixture. The nonvolatile fraction is about two-fifths resins (aromatic compounds soluble in pentane) and about three-fifths asphaltenes (complex aromatic molecules not soluble in pentane). Raw bitumen contains more aromatic multiple bond structures than conventional crude oils.

| Major Elements (Mass %) | Trace Elements (Mass %) |
|---|---|
| C 83.3 | V 0.025 |
| H 10.1 | Ni 0.010 |
| O 1.0 | Cu 0.0005 |
| N 0.5 | |
| S 5.0 | |
| **Density (20°C)** | **Molar Mass** |
| 1.02 g/ml | 500 - 800 g/mol |

*Chemical Composition of Bitumen*

**Sketch circle graphs to illustrate the proportions of:**

**1. major and trace elements in tar sands**

**2. alkanes, light aromatic, resins and asphaltenes in tar sands**

Bitumen is an incredibly complex mixture of large molecules, but for the sake of example, try this. Assume 100 g sample of a substance, *alchemoily*, with a molar mass of 712 g/mol. Analysis shows it to be 84.0% C and 10.1% H by mass. Ignore the remaining elements.

**Use this information to answer the following questions.**

**3. Calculate the mass of C atoms present.**

**4. Calculate the mass of H atoms present.**

**5. Calculate the number of moles of C atoms.**

**6. Calculate the number of moles of H atoms.**

7. Calculate the simplest whole number ratio of C to H atoms.

8. Calculate the molecular formula for *alchemoily* from the ratio in Question 7 and the known molar mass. Remember that 5.9% of the molar mass is due to elements other than C and H.

9. Discuss the feasibility of separating bitumen into separate compounds by fractional distillation.

10. If the 3.7 Gt of economically surface-mineable bitumen in the Athabasca deposit are processed, what masses of V, Ni and Cu could theoretically be recovered as by-products?

# History of Process Research

### History of Discovery

The existence of the oil sands was first reported by Peter Pond. In 1778, while exploring for the Hudson's Bay Company, he observed bitumen seepage from layers exposed by the erosion of the Athabasca River valley. Ten years later Alexander Mackenzie wrote about the usefulness of bitumen as a sealer for canoes. Since that time a constant series of experimenters and entrepreneurs have attempted to find an economical way of extracting bitumen from the sand. Oil sands research is a classic case of eliminating the 99% of ideas that do not work. While a total history is beyond the scope of this unit, it is recommended as supplementary reading for those students interested. The oil sands' history provides good insight into human persistence and/or foolhardiness given the possibility of a good profit.

### History of Research

In 1920 the Alberta Research Council (ARC) began a long-term study of the oil sands. The hot water separation method became the main work of Dr. Karl Clark. This method is now the basis for commercial production. Dr. Clark's work forms the primary reference material for the method. By 1948-49 the ARC was successfully demonstrating this process in a 455 tonne per day extraction plant at Bitumount. (See Figure 4.) The discovery of crude oil at Leduc in 1947 caused a drop in interest in oil sands which persisted until the early 1960s. At that time a rise in oil prices and concern about total reserves of crude oil returned attention to oil sands as an economic energy source.

### History of Commercial Development

In 1965 Great Canadian Oil Sands (GCOS) began construction of an oil sands plant and in 1967 began production. The plant now processes an average of 8500 tonnes of synthetic crude oil per day. Construction began in 1974 on the Syncrude plant and beginning operation in 1978. At peak the Syncrude plant produces 17 800 tonnes of synthetic crude daily. Further plants on the scale of the Syncrude operation will likely be built over the next two decades as the economics of construction and the value of product permit.

To give some idea of scale, the Syncrude plant processes some 8000 tonnes of tar sand per hour. The mining sites for GCOS and Syncrude total some 3000 hectares, which represents about 1% of the surface-mineable oil sands. Syncrude expects to operate for 25 years at the above rate on its present mining area.

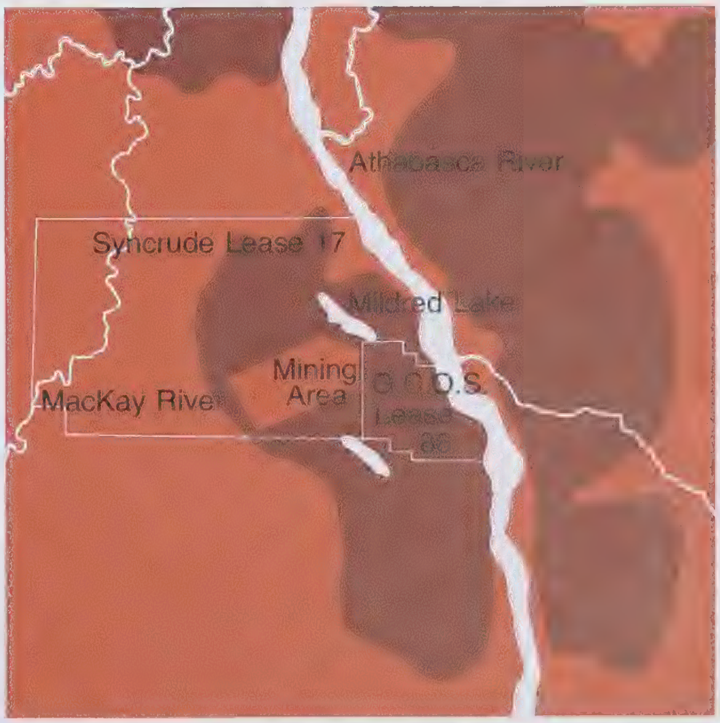


*Figure 7: Athabasca Deposit — Commercial Mining Area*

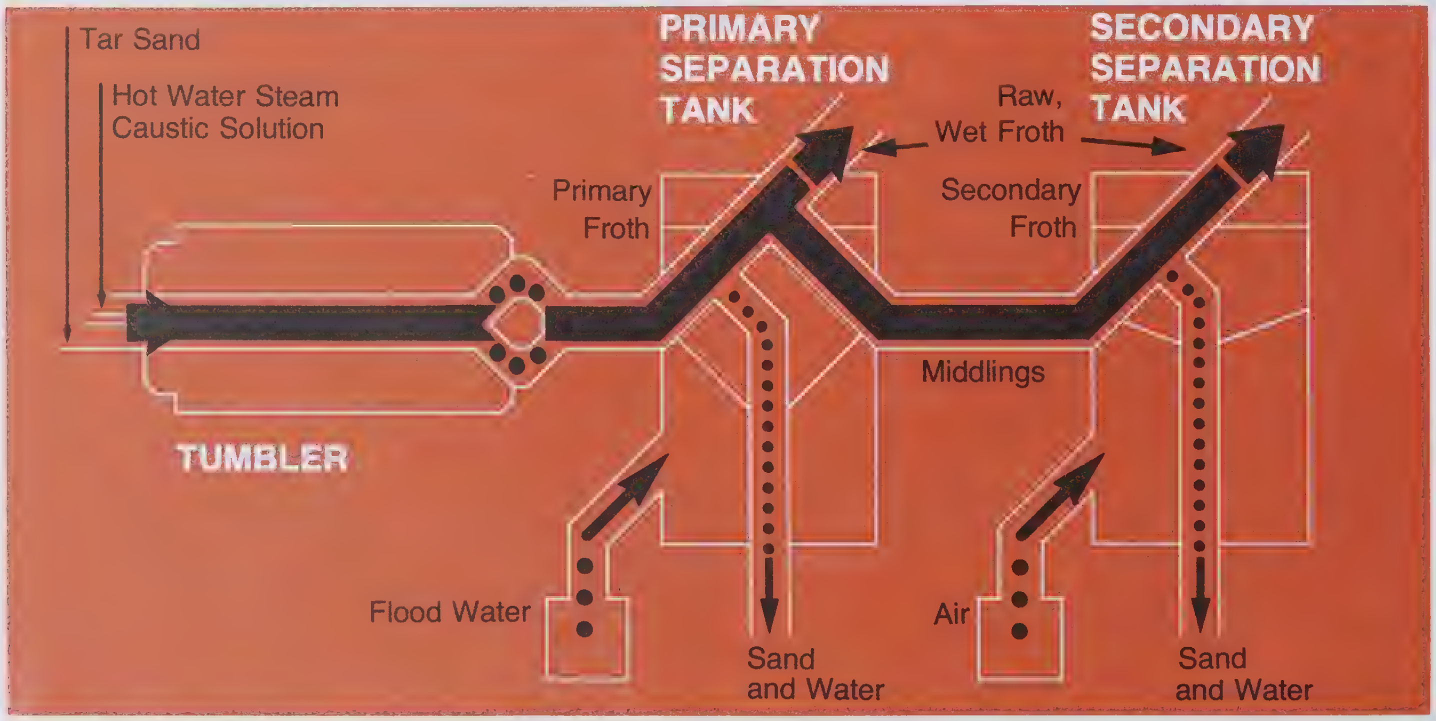
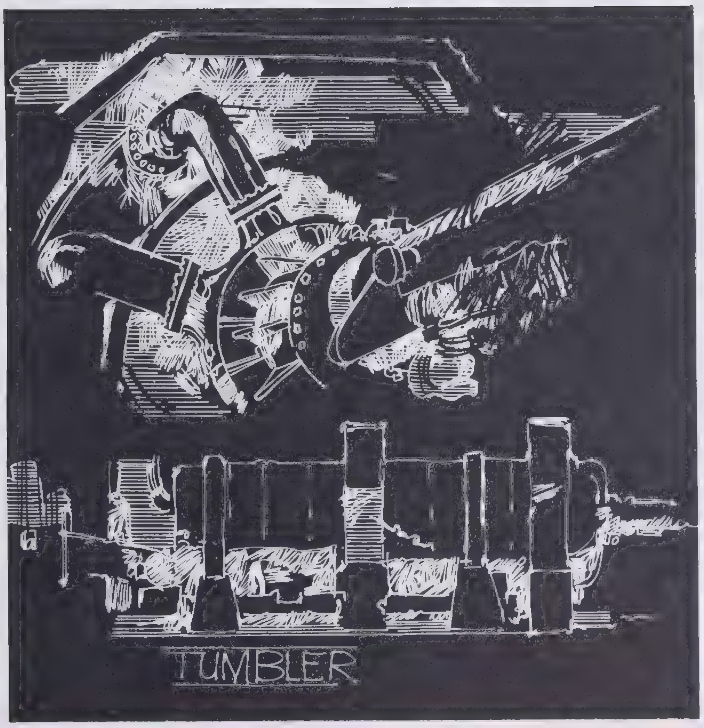


***Figure 8: Extraction of Froth***

# Extraction of Bitumen



Artist's Conception

### Slurry Preparation

In the initial extraction, freshly mined oil sand is agitated while water and steam are added. The mixture, a slurry, is about 0.3:1 water to sand by mass. Sodium hydroxide, $NaOH$, in about 1 M solution is added to raise the pH of the slurry from 7.0 to 8.5. The temperature rises to about 80°C in this mixing process. The water film between the bitumen and the sand grains (see Figure 6) ruptures, and small globules of bitumen froth form.

### Primary Froth Extraction

More hot flood water is added after the slurry moves to a primary separation tank, raising the water to initial tar sands mass ratio of about 1:1. In the primary separation tank, the heavy sand settles and is removed from the bottom. A layer of frothy, impure bitumen rises to the surface and is skimmed off. Between 75% and 90% of the bitumen is recovered in this primary froth.

### Secondary Froth Extraction

The water layer from the primary separation tanks still contains some bitumen and very fine solids. This water (middlings) layer flows to a secondary separation tank where agitation and air injection help separate the remaining bitumen as a secondary froth.

In summary the extraction of the bitumen as froth involves up to three steps.

1. Formation of a slurry in a rotating drum
2. Skimming of froth in a separation tank.
3. Further treatment of middlings to obtain more froth.

### Variables Affecting Bitumen Froth Extraction

The original water film around each sand grain is critical to the separation process. Samples of oil sand that have been exposed to air for some time give very poor bitumen separation. The bitumen in such samples is in direct contact with the sand due to migration of the water film. The effect of pH on separation was determined empirically, and is not well understood conceptually. The temperature control is important in that at temperatures below about 30°C bitumen is denser than water, but from 30°C - 100°C it will float on water.

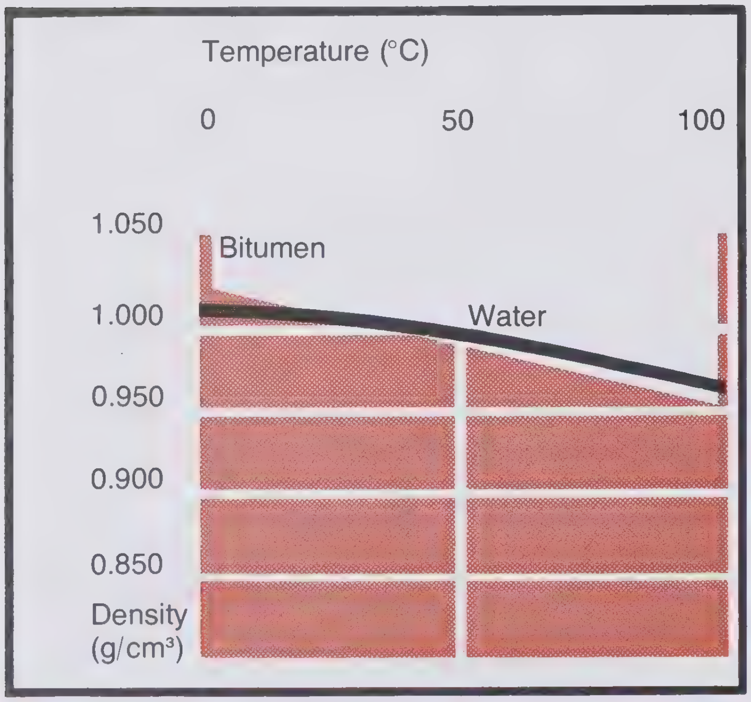


*Figure 9: Density of Bitumen and $H_2O$ vs. Temperature*

### Froth Treatment

The froth from primary extraction is about 60% bitumen. (The remaining 40% is mostly water plus some sand and mineral fines.) The froth is mixed with naphtha and centrifuged to remove the water and solid particles.

Naphtha is a term for a mixture of hydrocarbons composed of approximately $C_5$ to $C_7$ structures. Bitumen is soluble in such a mixture. The naphtha used to dissolve and thin the bitumen is recovered by distillation and is recycled.

### Tailings

About 50% of the water used in froth extraction is recycled from the tailings pond. The remaining tailings pond water cannot be recycled for this purpose because it contains fine mineral particles in suspension.

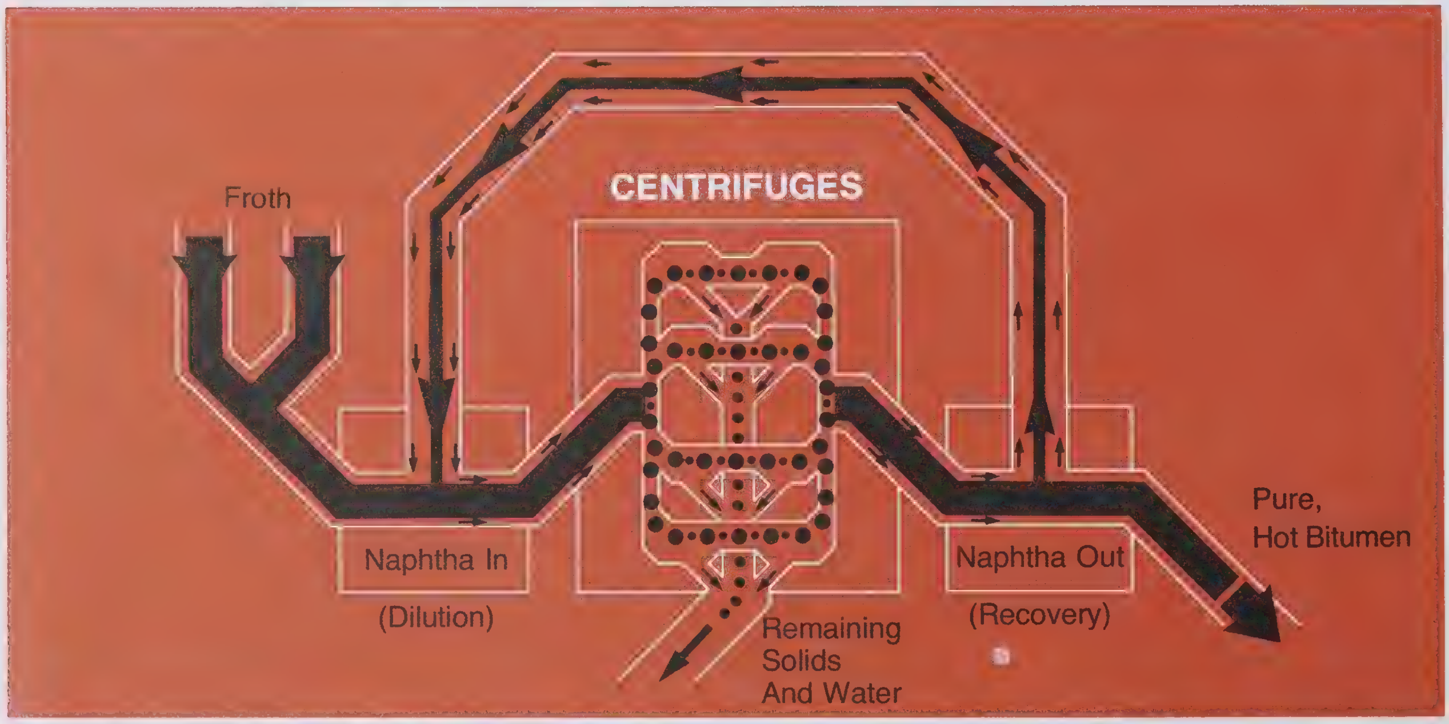


*Figure 10: Extraction of Bitumen From Froth*

# Extraction of Bitumen – Lab

**Purpose**

1. To perform and observe a hot water separation of bitumen from tar sand.
2. To observe differential settling of components in the tar sand/water mixture.
3. To observe the action of various solvents on extracted bitumen.

**Materials:**

Part A:
1-sample of tar sand (approximately 100 g)
1-ring stand
1-ring clamp
1-wire gauze
1-burner
1-400 ml beaker
1-pair beaker tongs
1-disposable stir stick
1-disposable transparent container 200-300 ml (transparent plastic party cups or small glass food jars are ideal)
1-dropping bottle 1.0 M NaOH
1-dropping bottle of phenolphthalein indicator
1-paper towel
1-plastic garbage bag (per class)
1-bucket (per class)

Part B;
1-laboratory waste container (metal or glass)
1-stock supply of bitumen
1-test tube rack
5-small (13 x 100 mm) test tubes
5-wood splints or stir sticks (disposable)
5 labelled dropping bottles containing:
1. $H_2O$ and detergent
2. acetone, $CH_3COCH_3$
3. ethanol, $C_2H_5OH$
4. toluene, $C_6H_5CH_3$
5. Varsol, naphtha or equivalent commercial solvent ($C_5$ to $C_7$ hydrocarbon mixture)

1 waste container, preferably metal, such as a tin can

**Procedure:**

Part A:

1. Place about 250 ml of tap water into the 400 ml beaker.
2. Add a few drops of phenolphthalein indicator to the tap water.
3. While stirring, add NaOH solution drop by drop to the water until the first persistent pink tinge appears.
4. Support the 400 ml beaker on the wire gauze and ring clamp and heat just to boiling over the burner.
5. Shut off the burner. ***Remember throughout this lab that the bitumen and solvents used are flammable and so are their vapors.***
6. Place a 100 g sample of tar sand in a disposable transparent container.
7. Place the container on a paper towel.
8. Using beaker tongs, pour enough hot water from the 400 ml beaker into the oil sand sample to make a thick slurry.
9. Stir (slurry) the sand/water mixture thoroughly for up to five minutes.
10. Add about 100 ml more hot water during the last moments of stirring to bring the water to the top of the container. Allow the contents of the container to settle. Record observations.

11. Use the stir stick to skim off the bitumen froth layer onto a paper towel.
12. Record observations about the odor, color and viscosity (thickness) of bitumen when it cools to room temperature.
13. Pour the water from the separation container into the bucket. Stuff the paper towel into the container (including sand and middlings) and dispose of the container into the plastic garbage bag.

## Observations:

**Part A:**

**1. Sketch the container and contents after settling and record observations about the appearance of the various layers. Label each layer.**

**2. Record observations about extracted bitumen at room temperatures.**

## Procedure:

Part B:

1. Obtain a sample of bitumen from the stock supply in the laboratory. Take a small spoonful on a paper towel to the station.
2. *Check that no burners are on in the laboratory.*
3. Add a different solvent to each test tube, to a depth of 2 - 3 cm.
4. Coat 1 cm or less of the end of a disposable wood splint with bitumen. Use as small an amount of bitumen as possible.
5. Place the coated end of the stick into one of the solvents and stir gently.
6. Repeat Steps 4 and 5 for each solvent in turn. Record observations as to the effect of the solvents on bitumen.
7. Using tightly rolled pieces of paper towel and Varsol, naphtha or equivalent commercial solvent, clean the test tubes.
8. ***Pour all used solvents into a tin can waste container. Do not pour flammable solvents into the sink.***
9. Dispose of the stir sticks and paper towels into the laboratory garbage container.

## Observations

### Part B

| Solvent | Total, Partial or No Solution |
|---|---|
| water ($H_2O$) and detergent | |
| acetone ($CH_3COCH_3$) | |
| ethanol ($C_2H_5OH$) | |
| toluene ($C_6H_5CH_3$) | |
| hydrocarbon mixture | |

Questions:

1. What is the approximate pH at the color change point of phenolphthalein?

2. In commercial secondary froth extraction, aeration improves the separation of bitumen. Discuss the possible reasons for this.

3. Sketch the sand layer to show gradation in size of particles and position occupied in the layer. Where are the very finest particles from the original sample?

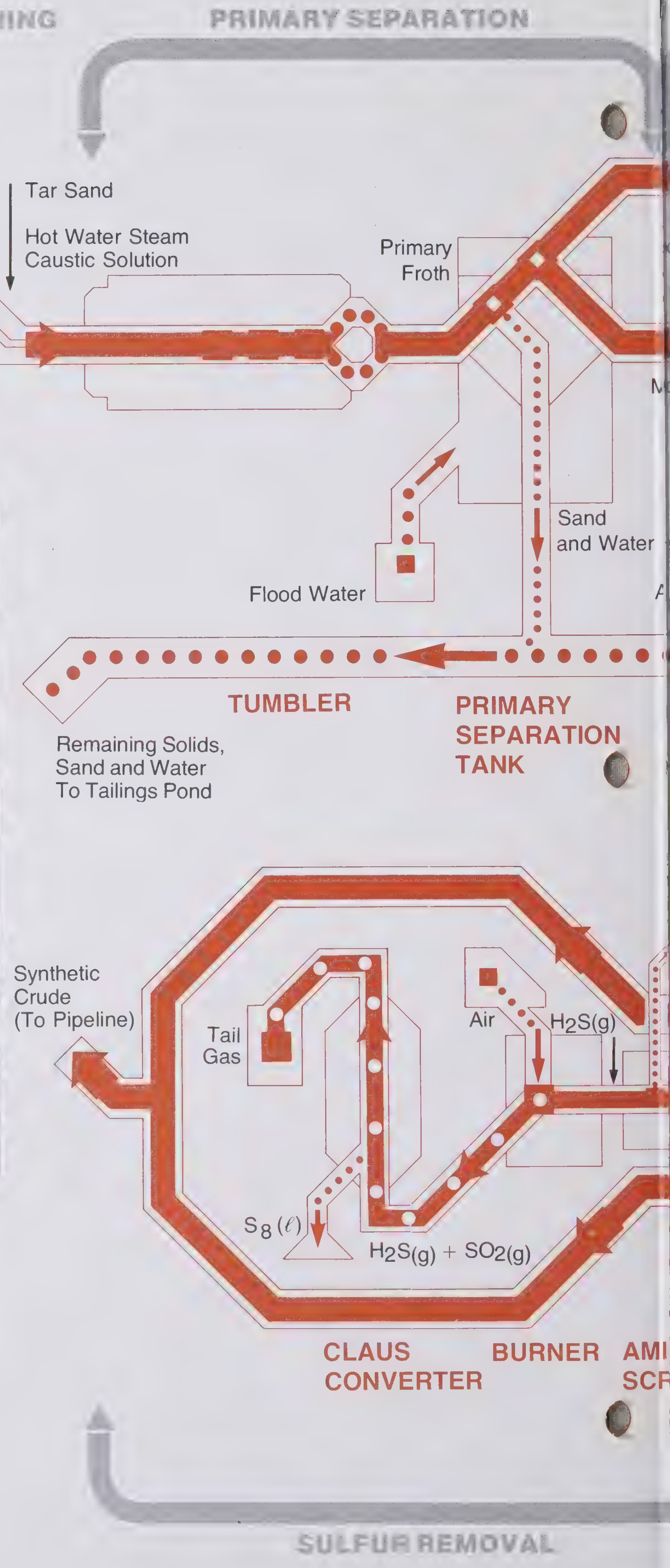
4. Based on observation of bitumen at room temperature, predict the ease of digging oil sand at -40°C.

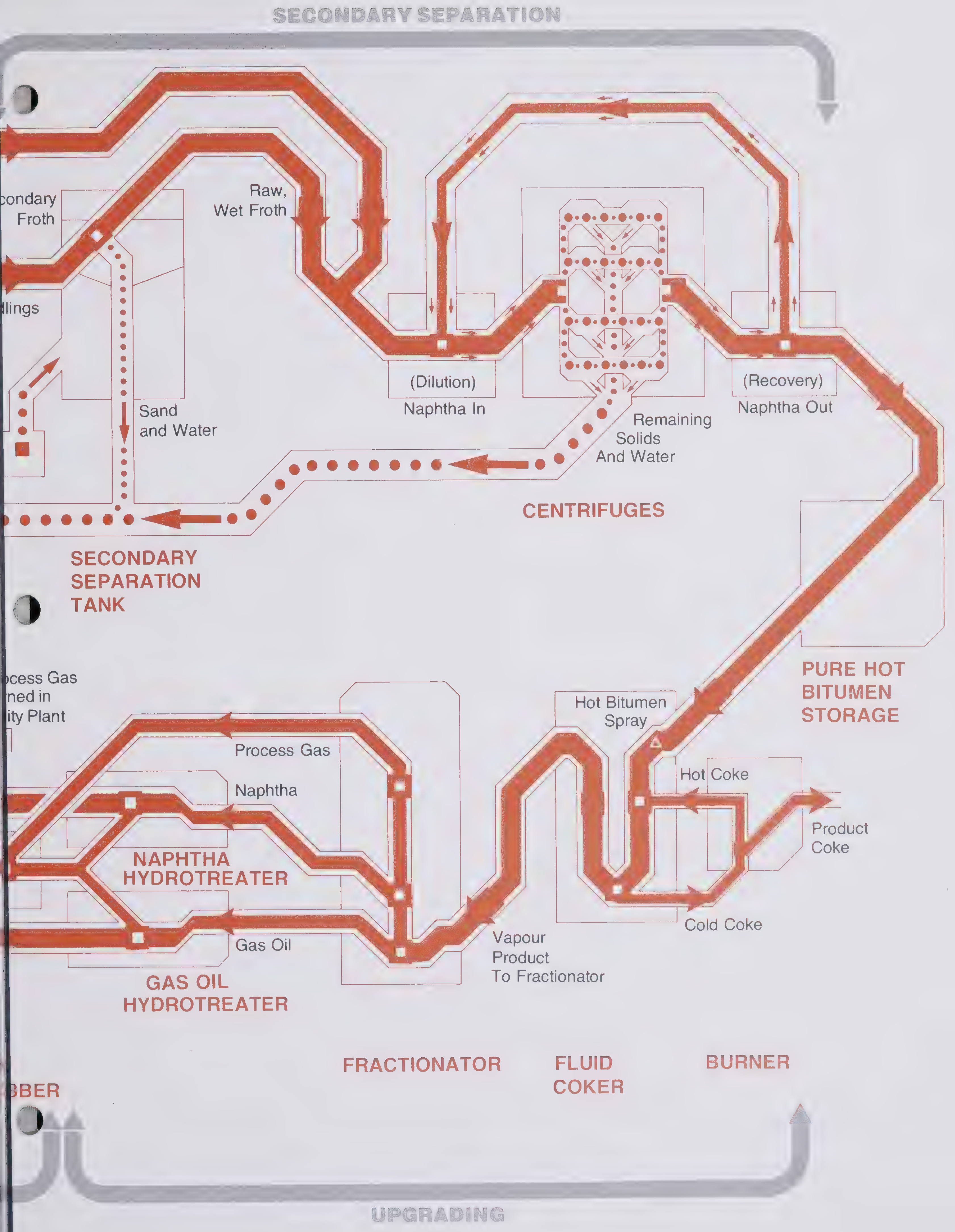
5. Why is it important to have the diluent recovery unit (flash tower) near the unit which will treat the pure bitumen?

The Athabasca Tar Sands

# Production Of Synthetic Crude Oil

This flow chart shows how synthetic crude oil is produced from tar sands mined from surface deposits north of Fort McMurray, Alberta. This process describes the principles underlying the operation of the Syncrude plant — the second commercial plant to be built in this region.




SECONDARY SEPARATION
condary
Froth
Raw,
Wet Froth
dlings
Sand
and Water
(Dilution)
Naphtha In
Remaining
Solids
And Water
(Recovery)
Naphtha Out
CENTRIFUGES
SECONDARY
SEPARATION
TANK
PURE HOT
BITUMEN
STORAGE
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ned in
ity Plant
Process Gas
Naphtha
NAPHTHA
HYDROTREATER
Gas Oil
GAS OIL
HYDROTREATER
Hot Bitumen
Spray
Hot Coke
Product
Coke
Cold Coke
Vapour
Product
To Fractionator
FRACTIONATOR
FLUID
COKER
BURNER
BBER
UPGRADING

6. The molecules in bitumen generally have both aromatic and aliphatic structure. Knowing this, could the "like dissolves like" rule be used to predict that one of the pure compound solvents in this lab would dissolve bitumen? Discuss this point and draw a structural formula for the compound.

7. Why would a commercial installation use a hydrocarbon mixture (naphtha) as a large scale solvent, rather than a pure compound?

8. Suggest an economic reason why bitumen is treated further on site, rather than being pumped to an existing refinery elsewhere in Alberta.

# Upgrading of Bitumen – Coking

### Molecular Structures in Bitumen

The original bitumen is about 20% mixed alkanes and cycloalkanes which probably occur as very complex branched chains. Consider that eicosane, $C_{20}H_{42}$ is known to have 366 319 different isomers, and that this is a simple alkane with no multiple bonds or cyclic structure. It is important to realize that in any fraction of bitumen there is no practical limit to the number of possible molecular structures.

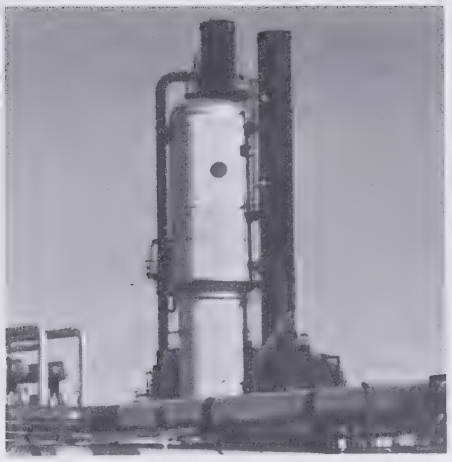
About 30% of bitumen is light aromatic compounds. These may be thought of as one or more benzene rings contained within a complex branched chain.

Another 20% of bitumen is resins. Resins are defined as being aromatic compounds which are soluble in pentane. These may be thought of as similar to a pyrene structure with most of the peripheral hydrogens substituted by carbon chains or further aromatic structures. About 65% of all C atoms in resins are in aromatic locations.

The final 30% of bitumen is asphaltenes. Asphaltenes are defined as being aromatic compounds which are not soluble in pentane.

These compounds are thought to resemble substituted dinaphthovalenes. Molar mass and insolubility in benzene suggest that each asphaltene molecule consists of three or more of these structures, connected by carbon chains and other substituted multiple ring aromatics.

The bitumen before coking has a hydrogen to carbon atom ratio of about 1.47 H/C. This can be used as a measure of the degree of aromatic



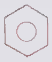
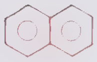
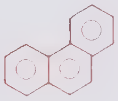
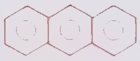
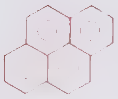
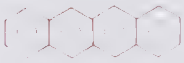
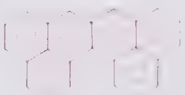
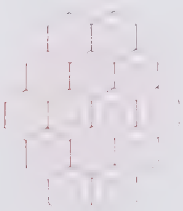
| Hydrocarbon | Structure |
|---|---|
| benzene |  |
| naphthalene |  |
| phenanthrene |  |
| anthracene |  |
| pyrene |  |
| naphthacene |  |
| dibenzonaphthalene |  |
| dinaphthovalene |  |

*Table 3: Some simple aromatic Hydrocarbons*

character of the material. Consider that pure aliphatic compounds have a ratio of about 2.0 H/C, and pure aromatics have a ratio of about 1.0 H/C or less

### Coking

The first step in converting extracted bitumen to synthetic crude oil involes subjecting the bitumen to a high temperature in a closed vessel. GCOS uses a delayed coking process in which the container vessel is sealed for a set time. The reaction is a batch-by-batch process. Syncrude uses a continuous flow fluid coking process in which bitumen is sprayed onto a bed of coke particles at a temperature of about 500°C.

The bed of hot coke particles in the fluid coking vessel gets progressively cooler from the surface to the bottom. Low-temperature coke is continuously withdrawn from the bottom and moved to a coke burner. High temperature coke from the burner is continuously returned to the surface of the coke bed in the fluid coker. The particles in the coke bed are kept separate and in constant motion by steam injection and by the agitating effect of vaporizing bitumen.

The lighter molecules in the bitumen vaporize, and the heavier molecules are cracked by the heat. Much of the material produced by cracking converts to smaller molecules which come off as a vapor. Some of the original bitumen is converted to coke. The process thus produces coke continuously. In fluid coking some of the product coke is burned to provide heat for the process, and some is withdrawn and stockpiled. The trace metals and fine mineral impurities in the original bitumen remain in the coke fraction produced. When this coke is burned these constituents are further concentrated in the ash.

Complete the following questions about the coking of bitumen. Refer to Tables 3 and 4 where necessary.

1. What is the molecular formula for pyrene?

2. How many side chains can be substituted on a pyrene group? On a naphthacene group?

3. What is the H/C ratio for dibenzonaphthalene? What is the molar mass?

Assume that the cracking of a bitumen molecule forms a phenanthrene group which then breaks its aromatic rings and forms a single alkane molecule. Use this assumption in Questions 4 to 8.

4. What is the molecular formula for phenanthrene?

5. What is the phenanthrene H/C ratio?

6. What is the molecular formula for the alkane formula?

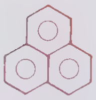
7. What is the H/C ratio of the alkane formed?

8. Could the alkane form as a straight-chain molecule or would it have to be branched? Explain.

9. Draw a structural formula for a naphthalene structure with a methyl, two ethyl and one propyl side groups. Calculate the molar mass of this molecule.

10. What is the maximum number of side chains that could be attached to a dinaphthovalene molecule?

11. Are phenanthrene and anthracene isomers of each other? Are either of them isomers of the structure below? Explain.



12. How many structures can there be containing only four aromatic rings? Which of the possible structures are isomers? Sketch structures and try to find the names of each one.

## Coking Products — Fractionator

The vaporized hydrocarbons emerging from the coker are separated into fractions by cooling and successive condensation. GCOS condenses three fractions as gas oil, kerosene and naphtha. Syncrude will condense two fractions as gas oil and naphtha. The fraction that does not condense at room temperature (20°C) is called process gas. This gas is treated to remove $H_2S$ and $NH_3$ and is then used as fuel on site.

Terms such as *naphtha* are not specific. They refer to complex hydrocarbon mixtures that have distillation temperatures within similar ranges.

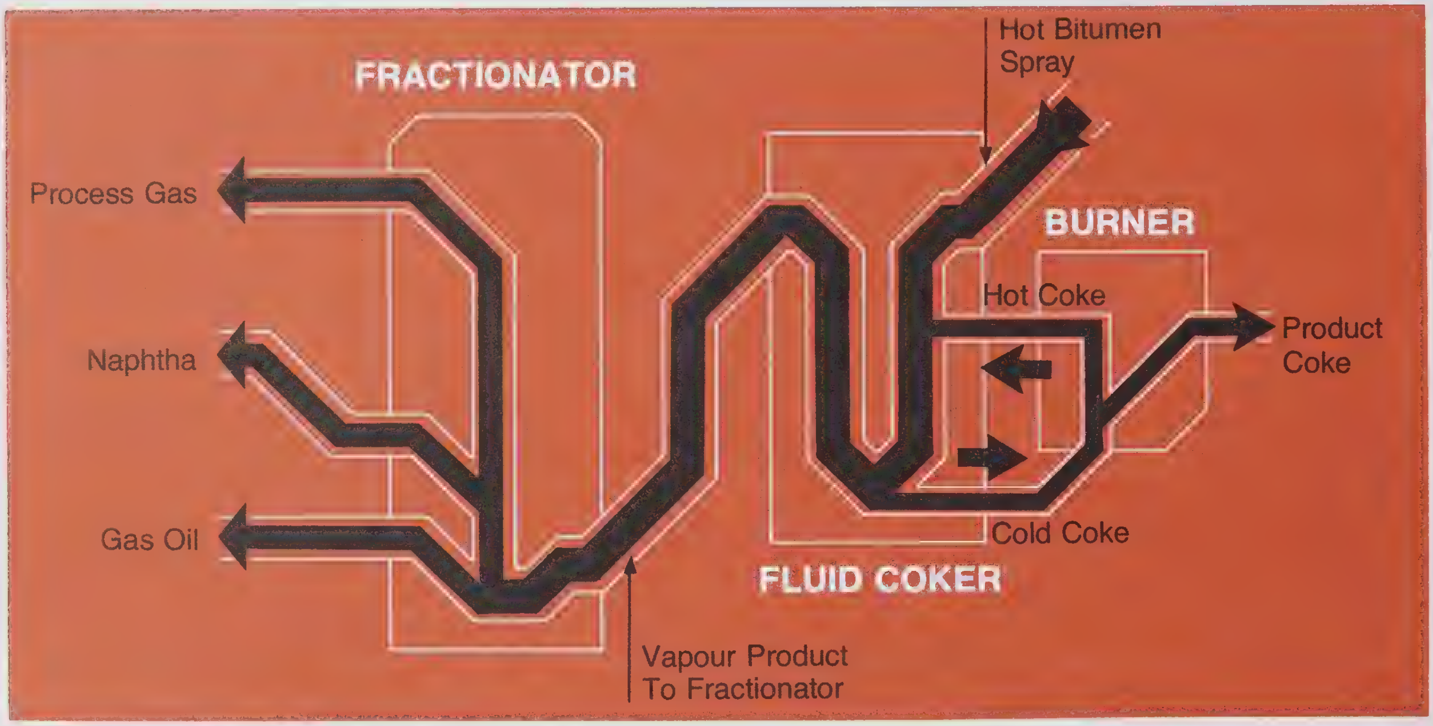
The following table will give an idea of the meaning of names applied to cracking fractions. Remember that all values are approximate and vary according to the producer and process used.

## Molecular Structures of Coking Products

The nature of changes during the cracking process is extraordinarily complex. However, a good idea of the molecular rearrangements can be obtained by analysis, extraction, infrared spectroscopy and similar processes.

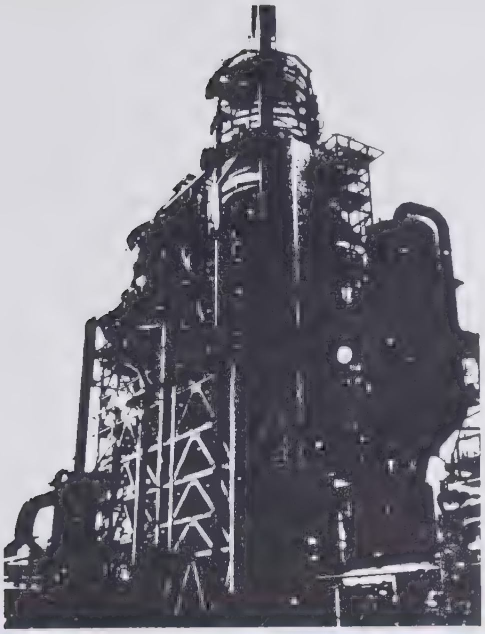
The coke residue may be thought of as a highly aromatic condensed network carbon structure. The H/C ratio in the *coke residue* is 0.59 - 0.77. The naphtha and gas oil liquid fractions have a ratio of 1.60 - 1.65 H/C, while the process gas fraction is equal to or greater than 2 H/C. In order to achieve these large ratios cracking must involve breaking of aromatic rings as well as breaking of chains. It is thought that a great deal of hydrogen transfer to and from multiple bonds and broken bond sites must occur. The larger the product molecules are, the greater their degree of aromatic character. Product per cent composition varies, but in delayed coking it is about 20% coke, 8% gas and 72% liquids. In fluid coking the final values are 10% coke, 11% gas and 79% liquids. (About 30% of the coke originally produced is burned during this process.) The molar masses of liquid products from coking range from about 70 to 250 g/mol.

***Figure 11: Fluid Coker***



| COKING FRACTION | BOILING POINT (°C) | CARBON NUMBER |
|---|---|---|
| process gas | <20 | 1 - 4 |
| naphtha | 20 - 200 | 5 - 11 |
| kerosene | 175-325 | 10 -16 plus light aromatics |
| gas oil | 275-524 | 12 and higher |
| coke | nonvolatile solids | very large aromatic molecules |

*Table 4: Petroleum fractions*



# Cracking Bitumen - Demo

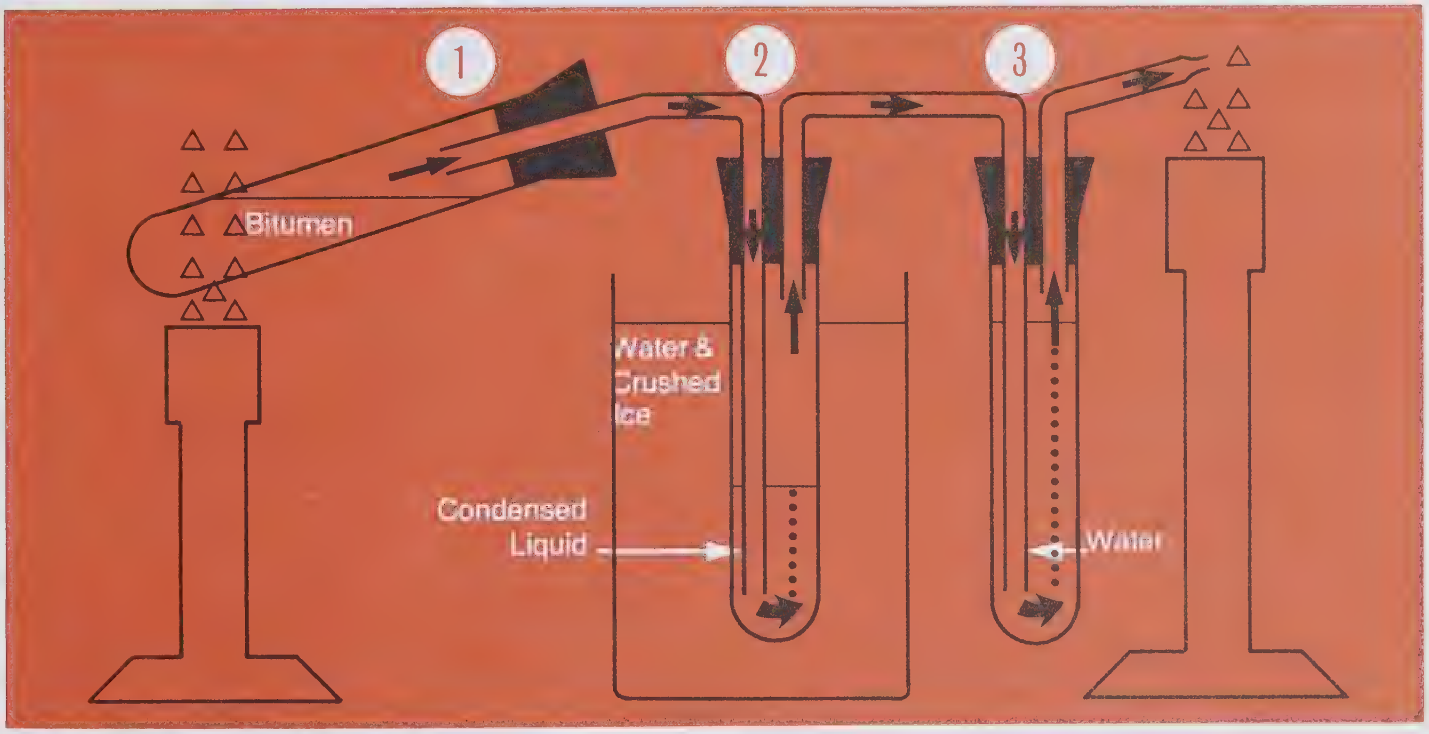


*Figure 12: Cracking Bitumen*

**Purpose:**

To parallel and illustrate the cracking of bitumen in the coking process.

**Materials:**

1-bitumen sample (about 5-15 g)
3-25 x 250 mm test tubes
stoppers to fit the above test tubes: 1-1 hole, 2-2 hole
1-triangular file
glass tubing (about 50 cm)
1-glass jet
2-burners (or 1 burner and 1 candle)
2-ring stands
2-utility clamps
1-600 ml beaker
crushed ice

**Procedure:**

1. Determine the masses of test tubes 1 and 2.
2. Add a sample of bitumen to test tube 1 and determine the mass again.
3. Assemble the apparatus as shown in the diagram. Points to note are:
   a. all seals must be tight
   b. inlet tubing to test tubes 2 and 3 should be no less than four-fifths of the depth of the test tubes
   c. the final jet opening should be small — about 1-2 mm diameter (thickness of a dime)
   d. the air space in test tube 3 (the water flashback trap) should be small — about 2-3 cm below outlet.
4. Light one burner and begin gradual heating of the bitumen.

5. After gas has evolved through the water trap for about a minute and initial air has largely been expelled, light the second burner (or candle) and place it by the jet outlet. It should keep outlet gases ignited as they are expelled.
6. When heating produces no further changes and gas is only very slowly evolved, ***shut off both burners and immediately remove the stopper from test tube 1*** to prevent backflow of liquids.
7. Record observations describing the nature of the liquid condensed in test tube 2.
8. After cooling, record observations describing the nature of the residue in test tube 1.
9. Determine the mass of test tubes 1 and 2 with their contents.

**Observations:**

**mass of test tube 1 . . . . . . . . . . . . . . . . . .**
**mass of test tube 1 and bitumen . . . . . . .**
**mass of test tube 1 and final residue . . .**
**mass of test tube 2 . . . . . . . . . . . . . . . . . .**
**mass of test tube 2 and final contents . .**

**Nature of liquid in test tube 2.**

**Nature of final residue in test tube 1.**

**Calculations and Questions:**

**1. Calculate the mass of bitumen in the original sample, and use this mass to find the mass per cent yield of solid, liquid and gaseous final products. Show all work.**

**2. List some ways this destructive distillation demo is similar to a coking process, and some ways that they differ.**

3. Describe a method for determining whether the solid residue has significantly different molecular components. (Hint: Re-read Part B, Lab)

4. Describe a possible method for collecting the liquifiable product as two or more fractions, using laboratory equipment.

# Upgrading of Bitumen — Hydrotreating

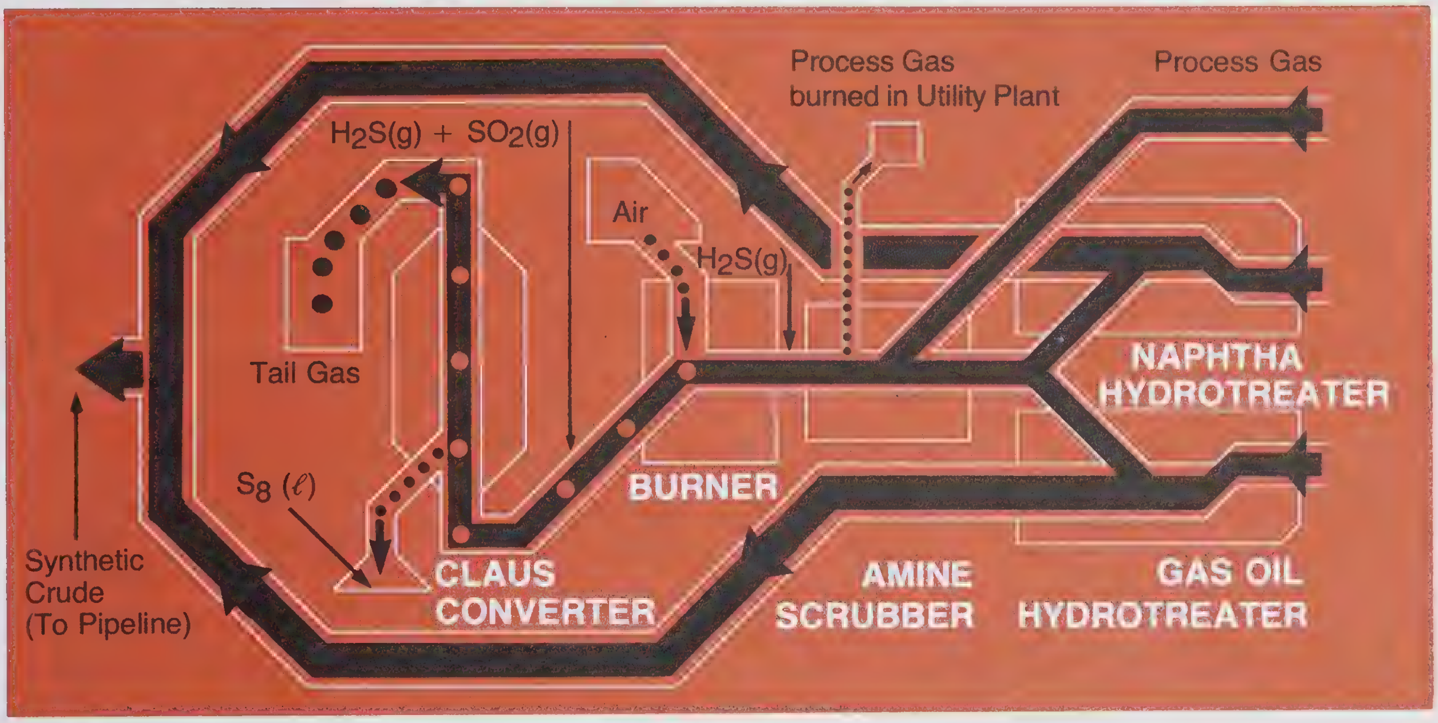


***Figure 13: Hydrotreating***

### Hydrotreating of Liquid Products

The liquid products from the coking step are treated for two basic reasons.

1. Impurities, especially sulfur and nitrogen, must be removed.
2. The liquids are unstable and will react to form unwanted viscous compounds unless treated further.

The process of hydrotreating involves reacting the liquid fractions separately with hydrogen at high temperatures and pressures. Temperatures can be 300 - 400°C and pressures from 5.0 - 10.0 megapascals (MPa) depending on the fraction being hydrotreated. The fractions are obtained and then treated separately because of the different conditions required for proper hydrotreating.

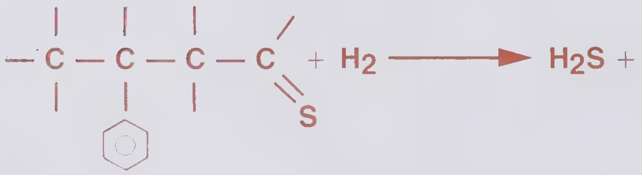
## Reactions that Remove Impurities

Most S, O and N atoms remaining in the molecular structures are combined with and replaced with H atoms during hydrotreating. They are removed as $H_2S$, $NH_3$, and $H_2O$ vapors from the gases formed in the reactions.

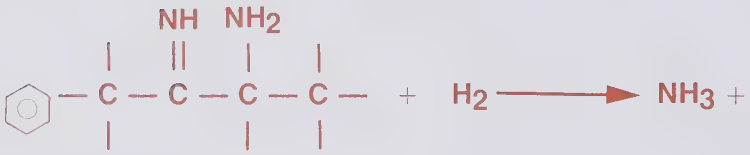
The following questions illustrate, in a general way, the reactions that remove the impurities.

**Complete the following structural equations. Determine the number of moles of hydrogen required in each case and name the organic products. (Hydrogen both replaces and combines with the atom or atoms shown as impurities.)**

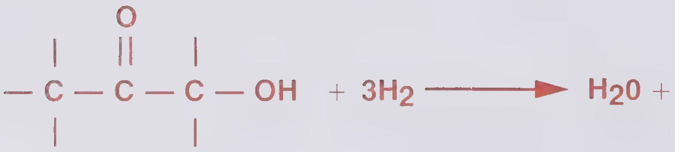
1.



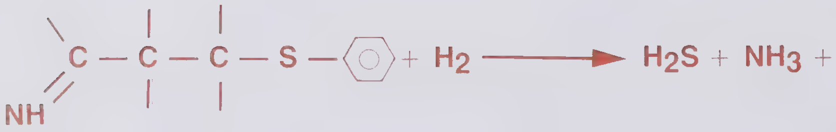
2.



3.



4.



**5. One of the organic products formed in the reaction in Question 4 will not liquefy upon cooling to room temperature. Name the product.**

## Stabilization Reactions

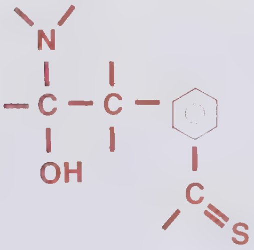
A significant amount of hydrogen is used up in addition reactions which convert multiple bonds to singles. More is consumed in partial saturation or aromatic structures. The degree of saturation can be controlled by varying time, temperature and pressures. This part of the process tends to produce stable liquid products that will not change composition. It is important that a liquid not form, say, paraffin waxes, halfway along a pipeline.

**The following questions illustrate, again very generally, the nature of hydrogen addition reactions in hydrotreating.**

**6. Write and balance an equation using structure formulas for the conversion of $CH_2CHCHCH_2$ (1,3-butadiene) to an alkane by $H_2$ addition.**

**7. Write and balance an equation for the conversion of $C_6H_5CH_2$ (toluene or methylbenzene) to an alkane by $H_2$ addition.**

**The compound below may react with $H_2$ to form a single straight-chain alkane.**



**8. Write a balanced equation for the reaction.**

**9. Calculate the yield of each product and the $H_2$ consumed in kilograms if 1.00 t of the above compound were to react in this way.**

Hydrotreating yields lighter, less dense products than the original feed material. This is partly due to saturation and partly due to breaking of some molecular structures. The products are again separated into fractions by condensation and stored, to be recombined later into a common liquid called synthetic crude. Actually the term *synthetic* is a misnomer. The liquid can be used as a feedstock in refineries in much the same way as any conventional crude oil. Synthetic crude requires less heating than many so-called conventional crudes and has higher aromatic content, but it is not synthesized in any chemical sense.

**A good discussion question here might be: why are the liquid fractions recombined before piping to refineries? After all, the first thing refineries do to feed oil is fraction it into many separate streams.**

# Ancillary Reaction Units

### Hydrogen Generation

The hydrogen used in the hydrotreating process is produced by reacting natural gas with water vapor at high temperature and pressure. The methane and ethane in the natural gas react with $H_2O$ to form hydrogen and carbon dioxide. The $CO_2$ is separated and vented to the atmosphere.

**1. Write equations for the reactions of methane and ethane with water vapor to produce $CO_2$ and $H_2$.**

**2. Assume natural gas is 90% methane and 10% ethane. How many kilograms of hydrogen can theoretically be produced from 1.00 t of natural gas?**

## Amine Scrubber

Process gas produced in coking and hydrotreating units is contaminated with hydrogen sulfide gas, which must be removed before using the hydrocarbon gas mixture as fuel. $H_2S$ is both corrosive and poisonous, with a toxicity approaching that of hydrogen cyanide. By law, no $H_2S$ may intentionally be released into the atmosphere by any industrial process.

The most common method for removing $H_2S$ from hydrocarbon gases, including conventional natural gas, is by using an amine scrubber unit. The process involves selective reversible absorption of $H_2S$ in an aqueous solution of an amine, diethanolamine ($HN(C_2H_4OH)_2$). The amines most used are monoethanolamine (MEA), diethanolamine (DEA) and diisopropanolamine (DIPA). The Syncrude scrubber uses a 20 to 25 per cent aqueous solution of DEA.

The hydrogen gas mixture containing $H_2S$ (sour gas) is reacted with the aqueous amine under high pressures, on the order of 3 MPa to 6 MPa. The reaction that takes place is a Bronsted-Lowry acid-base reaction, with the amine acting as a base and $H_2S$ as the acid. Under high pressure conditions, this reaction is heavily favored. The hydrocarbon gases are not soluble in the solution and do not react with the DEA. The pressure is then decreased and the solution heated to remove $H_2S$. At low pressure and high temperature the original reaction reverses, and DEA and $H_2S$ are heavily favored as products. At high temperature $H_2S$ is not very soluble in water, so it is given off as a gas, which is removed. The DEA may now be reused in further cycles.

**1. Write a reaction equation using structural formulas for DEA reacting with $H_2S$. Show all species as aqueous. (A single proton is transferred to the N atom.)**

2. Use a Lewis diagram to show the electron distribution around the N atom after DEA has gained a proton.

3. What *molecules* on the *ALCHEM* acid-base table gain protons to become positive ions? Which of them is most similar to DEA? Explain.

4. Use the molecular formulas to rewrite the reaction equation from Question 1 again. Use double arrows to emphasize reversibility and showing which side is favored by which temperature and pressure conditions.

5. Using polarity and solubility theory, discuss why ethanol or isopropanol (2-propanol) substituted amines are used in this process.

6. Why would a simple aqueous ammonia solution not work in this process?

7. Draw a structural formula for DIPA. (isopropanol is the common name for 2-propanol.)

## Claus Converters

The $H_2S$ generated in the upgrading of bitumen is reacted in units called Claus converters. The $H_2S$ is first partially burned to generate water vapor and $SO_2$. The proportions of $SO_2$ to unreacted $H_2S$ are very carefully controlled. In the second stage, the remaining $H_2S$ and the $SO_2$ from stage 1 are reacted to form sulfur and water. This stage must be controlled so that there may be a slight excess of $SO_2$ or $H_2S$ in the product vapors, but one way the elimination of $H_2S$ is achieved is by burning the final gases in a flare stack. This converts any escaping $H_2S$ to $SO_2$. The sulfur vapor produced is removed by condensation.

It solidifies from vapor upon cooling. The sulfur at the tar sands plant is stockpiled as current prices make it uneconomical to transport or sell.

1. Write an equation for the combustion of $H_2S$ to $SO_2$ and water vapor.

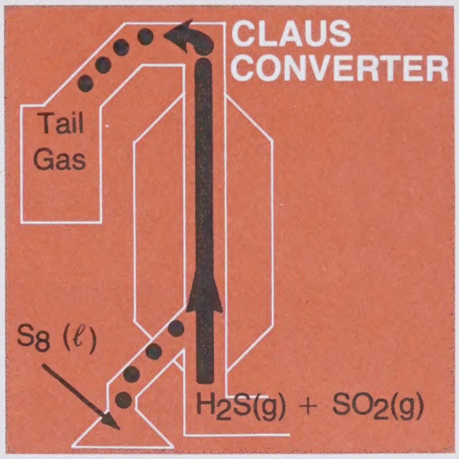
2. Write an equation for the combustion of $H_2S$ to sulfur vapor and water vapor.

3. Write an equation for the reaction of $H_2S$ with $SO_2$ to produce sulfur vapor and water vapor.

4. In the reaction of $H_2S$ and $SO_2$ what is the ideal percentage mole ratio of $H_2S$:$SO_2$? What is the ideal mass ratio?

5. What per cent by mass of a molecule of $H_2S$ is the sulfur atom?

6. What mass of sulfur could be produced by total reaction of 1.00 t $H_2S$?


CLAUS CONVERTER
Tail Gas
$S_8(\ell)$
$H_2S(g) + SO_2(g)$

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